COMPOSITE ANODE - SUMMARY OF 1982 WORK

1. Composite anode (stoichiometeric ratio of alumina and carbon) approach eliminates the dependency of the electrolysis on the alumina solubility in the Hall cell electrolyte. Thus providing for a flexibility of electrolyte choice, and accordingly allows for low temperature operation.

    -- The concept has been verified by carrying out a potentiostatic anodic measurements, where conventional carbon anode was found to reach a limiting current at or below 0.1 Amp/cm². While composite anode showed no current limitation up to 15 Amp/cm².

    -- Electrolysis experiments and data analysis of cell voltage components (using simple model) has demonstrated that a power consumption of about 4 kWh/lb Al is achievable using composite anode at the conventional current density (0.75 Amp/cm²) or equal power consumption to conventional cells (i.e. 6 kWh/lb Al) at double the current density. These results were obtained experimentally using a 3" diameter composite anode, both all fluoride melt and a mixed halide electrolyte, at electrolyte temperature of about 750^{O}C and an ACD of 1".

2. The acceptable electrolyte for the composite anode should meet the following properties characteristics = low liquidus temperature

($\leq 850^{0}$C), high conductivity ($\geq 2\ \Omega^{-1}\ cm^{-1}$), relatively low vapor pressure, moderately low solubility of alumina, a density lower than aluminum and acceptable cost. Experiments were conducted to optimize a melt relative to the first three properities. A melt composition of a NaF/AlF_3 ratio of 1.0 with added LIF in the range of 5-10 wt % and NaCl of 0-10% was found to be acceptable. Liquidus temperature of $< 850^{0}$C and electrolyte conductivity of $3.5\ \Omega^{-1}\ cm^{-1}$ were achieved and because of the low operating temperature it is expected that these melts will have a relatively low vapor pressure.

3. Mechanically and electrically good composite anodes were initially made using Pora technology i.e. using stoichiometeric ratio of alumina and carbon, where the major source of carbon was phenolic compounds. However, the cost of phenolic makes this approach unacceptable economically. Initial attempts to use pitch or pitch and coke binder as the source of carbon failed to produce good anodes. The major reason for this behavior was the absorption of pitch on and in the alumina leaving little pitch binder to hold the anode together. A modification to the alumina either by treatment or type solved this problem. Heat treatment of the alumina producing a low surface area and high alpha content product resulted in good composite anodes with a pitch binder. Similarly, good mechanical and electrical composite anodes were produced using fully calcined ACH and Pechiney floury alumina with a pitch as the binder. These anodes had the properities of being rich in pitch; accordingly it is expected that using these alumina's, some of this pitch content can be substituted by coke.

This will reduce the total cost of the composite prebaked anode. A patent invention is being prepared on the use of various alumina's in producing economical anode which also opens up a potential market area of pitch bound refractories.

4. Prebaked composite anode cell material balance was carried out to determine the performance characteristics of the anode. Extended electrolysis runs using all pitch composite anode 3" Ø were conducted and results showed that (1) the anodic current efficiency was between 84-108%, with a cathodic current efficiency of almost 100%. This indicates that most likely there should be no problem in anode utilization in scale-up, (2) cell voltage, corrected for 1" ACD, met the program goal of 2.73 volts at 0.72 Amp/cm², accordingly the power consumption goal of 4 kWh/lb is believed to be achievable, (3) there was no chlorine evolution at the anode, when using melts containing chlorides. Accordingly, low-cost melts containing chlorides to depress the melting point and increase conductivity appear feasible for the composite anode process.

5. A prebaked composite anode requires in addition to the conventional carbon plant, to heat the alumina to the baking temperature. It also requires to handle 3-5 times more anodes than conventional carbon anodes. Thus, a concept analogaus to Soderberg approach was proposed. Tests were conducted using alumina and pitch in a simulated self-baked apparatus and results indicated that anodes produced by baking at 750°C were highly resistive (about 150 times more resistive than

prebaked composite anodes). The low baking temperature (conventional baking temperature is about $1000^{o}C$), is dictated by the electrolyte temperature, and in the case of composite anode electrolyte it is anticipated to be below $850^{o}C$ and typically $750^{o}C$. Accordingly, without an external supply of heat to the self-baked anode the IR potential drop will be sufficiently high to overcome any voltage advantage to the composite anode use.

6. Another composite anode concept was investigated to overcome the need to heat the alumina feed to the baking temperature and to avoid the handling problem of the prebaked anodes. This concept was to use alumina and coke particles as the anode. Results of a series of experiments using conductive and non-conductive separators to contain the composite anode particles indicated that (1) the major cell voltage losses in the composite particle is due to resistivity losses between particles and the IR drop at the separator (2) the cell voltages obtained, were a strong function of the static pressure on the particles. At a current density of 0.75 Amp/cm^2, a cell voltage of 8.3, 4.5 and 4.3 volts were obtained for a pressure of 0, 2 and 4 psi. Even though the last cell voltage is higher than the goal (2.73 volt) the results were very encouraging that the problem of high cell voltage is believed to be solvable. Thus, the key technical problem is believed to be the separator. Work is now being carried out at ARCO corporate to address the resistivity of the particle and the separator materials.